THERMOMAGNETIC INVESTIGATIONS OF PROMOTED AND UNPROMOTED IRON OXIDE AND IRON CATALYSTS*

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Thermomagnetic Investigations of Promoted and Unpromoted Iron Oxide and Iron Catalysts*

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The Curie temperature (θ) and intensity of magnetization of certain unreduced and reduced iron oxide catalysts have been determined. For the singly promoted unreduced systems of Fe_3O_4 containing small amounts of one of the following, Na_2O, K_2O, CaO, BaO, B_2O_3, Al_2O_3, or SiO_2, θ was found to be practically the same as for Fe_3O_4, but large reductions in the saturation intensity of magnetization (I_s) were observed. The doubly promoted unreduced systems studied contained additions to Fe_3O_4 of Al_2O_3 and one of the following (in small amounts): Na_2O, K_2O, BaO, or SiO_2. θ for these materials varied only slightly and was either equal to or less than that for Fe_3O_4. Large reductions in I_s were found. Magnetic measurements on the reduced materials gave values of θ the same as for pure iron. The extent to which the promoters go into solid solution, both for the unreduced and reduced materials, is determined. Additional unreduced unpromoted iron oxides were investigated that had variable ratios (γ) of Fe^{++}/Fe^{+++}. Starting at $\gamma=0.352$, I_s was found to increase with increasing γ to a maximum at $\gamma=0.50$, agreeing with the known value for magnetite, and then to decrease to a small value for large γ. The value found for I_s at $\gamma=0.352$ is in agreement with Néel's theory of "ferrimagnetism" as applied to cubic Fe_2O_3 and Fe_3O_4. θ was found to be constant at about 583°C for γ from 0.352 to 1.276.

I. INTRODUCTION

A KNOWLEDGE of the location of promoters in iron oxide and iron catalysts contributes greatly to the understanding of the nature of promoter action in catalysts. In the case of the singly promoted unreduced iron oxide catalyst, $Al_2O_3+Fe_3O_4$, two questions can be asked: first, where is the Al_2O_3 located before the iron oxide catalyst is reduced to the state of iron; and secondly, where is the Al_2O_3 located after reduction? The significance of the first question comes from the well-known fact that the previous history of a catalyst plays an important role in its catalytic activity.

It has been considered likely that in the preparation of a fused oxide catalyst, the Al_2O_3 promoter goes into solid solution with Fe_3O_4. The x-ray diffraction investigation of Wyckoff and Crittenden[1] supported this conclusion.

The second question was studied by Brill[2] who showed that in the reduced catalyst the aluminum is in the form of extremely finely divided Al_2O_3—the crystal size was estimated at probably less than 10^{-6} cm on a side.

Another approach to these problems can be made by thermomagnetic investigations. The way in which the saturation intensity of magnetization varies with temperature can provide information concerning the location of the promoters in these catalysts. The present paper describes thermomagnetic studies of certain catalysts prepared (1919–1926), at the Fixed Nitrogen Research Laboratory of the U. S. Department of Agriculture.

II. EXPERIMENTAL METHOD AND PROCEDURE

A photographic method similar to that described by Dejean[3] was used to record the thermomagnetic data. A small spot of light traversed the surface of a photographic paper which was held stationary. The motion of the spot of light was produced by two mutually perpendicular displacements, one proportional to the intensity of magnetization, the other proportional to the temperature of the sample. The trace, thus formed gives the intensity of magnetization as a function of the temperature, expressed by a curve in a rectangular two-coordinate system.

The ferromagnetic specimens placed in a strong magnetic field H, having a constant $\partial H/\partial x$, were acted upon by a force F, in the x direction of an amount

$$F=(\partial H/\partial x)I_sV, \qquad (1)$$

where V is the volume of the material, I_s the saturation intensity of magnetization. A linear relationship between F and I_s was realized approximately by constructing an electromagnet containing pole pieces that gave a constant $\partial H/\partial x$ in a region where H was large.

Figure 1(a) shows a sketch of a longitudinal cross section taken through the ends of the circular pole pieces used. The nature of the magnetic field obtained by such an arrangement is illustrated in Fig. 1(b). This spacial distribution of magnetic field intensities is in agreement with the data obtained by Buehl and Wulf[4] for similar pole pieces.

Powdered unreduced material was contained in a small platinum capsule,† held between the pole pieces of the electromagnet by means of an alundum tube which was suspended by a small torsion rod. For the reduced catalysts, the material was held in an atmosphere of nitrogen within a glass capsule.

On application of the magnetic field, the resulting

* Supported in part by the ONR.

[1] R. W. G. Wyckoff and E. D. Crittenden, J. Am. Chem. Soc. 47, 2866 (1925).

[2] R. Brill, Z. Elektrochem. 38, 669 (1932).

[3] P. Dejean, Ann. Physik 18, 171 (1922).

[4] R. Buehl and J. Wulf, Rev. Sci. Instr. 9, 224 (1938).

† Demagnetization fields, not amenable to computation, existed so that Eq. (1) is only approximate. Calibration tests, however, made with nickel and iron, showed that Eq. (1) proved to be sufficiently correct for the determination of Curie temperatures.

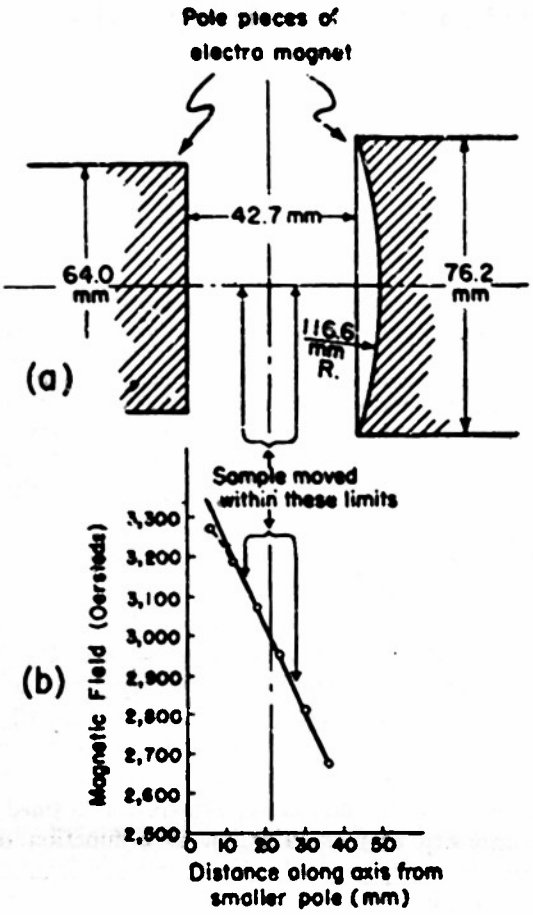

FIG. 1. Diagram illustrating the shape of the pole pieces used and the variation in the intensity of the magnetic field.

torque twisted the torsion rod, thereby rotating a plane mirror (M) mounted on the axis of the rod. The angular displacement of M was directly proportional to the forces acting on the sample.

Specimen temperatures were determined by means of a calibrated thermocouple arrangement with the hot junction held in contact with the capsule. The angle of rotation of a galvanometer mirror (N) in the thermocouple circuit was, therefore, proportional to the temperature of the specimen.

The specimens were heated by a cylindrically shaped furnace noninductively wound with nichrome V wire having a magnetic permeability of about 1.001. Heat insulation was obtained by using radiation shields. This compact furnace with one end open could be slid around the specimen and fitted between the pole pieces. The time required to heat the samples through the Curie temperature varied from 30 to 40 minutes.

The mirrors M and N were arranged in an optical system suitable for tracing out the thermomagnetic curves as described previously.

III. EXPERIMENTAL TESTS OF APPARATUS AND PROCEDURE

Preliminary runs on pure nickel.—A sample of nickel (No. N24), with a total amount of impurities of 0.067 percent, was kindly furnished by Mr. Harold E. Cleaves of the National Bureau of Standards for calibration purposes. Figure 2 shows a typical curve obtained for this material. Six runs were made on a sample held in an atmosphere of nitrogen which gave a Curie point of 369±1°C, while three runs on a second sample in air gave the same value. From Stoner[8] we find the Curie point $(\theta)_H$ of nickel in a field of H (in oersteds) given by

$$(\theta)_H=(\theta)_{H=0}+0.20(H^{\frac{1}{2}}), \qquad (2)$$

where reliable data give $(\theta)_{H=0}$ varying from 357.6°C to 360°C. If we take $(\theta)_{H=0}$ as 359° then from Eq. (2) we have for comparison with the present data a value of $(\theta)_H=370°$ for $H=3000$ oersteds. The agreement is within the experimental error.

Preliminary runs on pure iron.—Two different samples of iron having high purity were also furnished by Mr. Cleaves. One piece was from a quantity identified as No. 1 electrolytic iron ingot 8X, while the other was from ingot No. 9. Total amount of impurities were given as less than 0.009 percent. Eleven runs were made on three different samples of ingot No. 9 in air which, when averaged together, gave a Curie point of 780 ±1.6°C. Three runs in air, one by cooling, were made on a sample from the electrolytic iron which gave a Curie point of 779±1.3°C. Previous determinations, given in the literature, vary from 760 to 780°C (see reference 5) including changes in the Curie point due to existing magnetic fields. Pruess, for example, found a θ_H for iron of 774°C at $H=10{,}000$ oersteds. The present values found for iron appear slightly higher than was expected. The agreement, however, is considered satisfactory since, surprisingly, there appears to be no accurate value for reference in the case of iron.

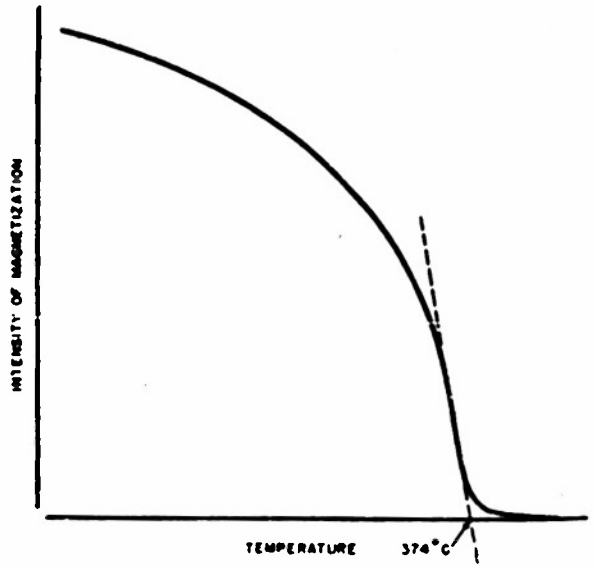

FIG. 2. A thermomagnetic curve obtained for a sample of pure nickel for calibration.

[8] E. C. Stoner, *Magnetism and Matter* (Methuen and Company, Ltd., London, 1934), pp. 383–4.

IV. RESULTS ON UNREDUCED CATALYSTS

Singly Promoted

Figure 3 shows typical records made on Fe_3O_4, Fe_3O_4 containing 20 mole percent Al_2O_3, and Fe_3O_4 containing 35.4 mole percent Al_2O_3. The temperature at which these materials lose their magnetization is roughly the same, but their intensities of magnetization are considerably different. Figure 4 illustrates other runs taken with other types of promoters. The same general behavior exists. For the case of the doubly promoted catalyst containing 6.02 mole percent Al_2O_3 and 0.80 mole percent BaO, the intensity of magnetization is about one-tenth that of Fe_3O_4, but the Curie point has not been greatly changed. It is apparent from these data that these materials show greater variation in their intensities of magnetizations than in their Curie temperatures.

The present apparatus was not designed for quantitative determinations of the intensity of magnetization;

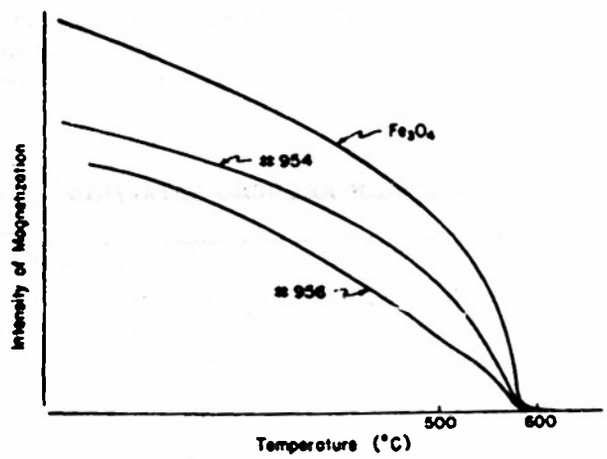

FIG. 3. Typical thermomagnetic curves for Fe_3O_4 and two singly promoted (Al_2O_3) unreduced catalysts Nos. 954 and 956 having 20 and 35.4 mole percent of Al_2O_3 respectively.

however, a procedure was adopted to obtain this information. A number of carefully weighed samples of unreduced catalysts, covering a wide range of intensities of magnetization, were submitted to Mr. R. L. Sanford of the National Bureau of Standards, who furnished accurate values for their intensities of magnetization. This information was obtained at an effective magnetizing field of 3000 oersteds. These samples were then used to calibrate the force deflections of the present apparatus so that the intensity of magnetization could be obtained for all of the remaining materials.

A summary of the data obtained for the singly promoted unreduced catalysts is shown in Table I. A number of different oxides have been used as promoters. Catalyst No. 956, containing about 35 mole percent of Al_2O_3, represents the case of the greatest amount of added promoter. The most striking fact shown by Table I is the constancy of the Curie point with corresponding large variations in the intensity of magnetization.

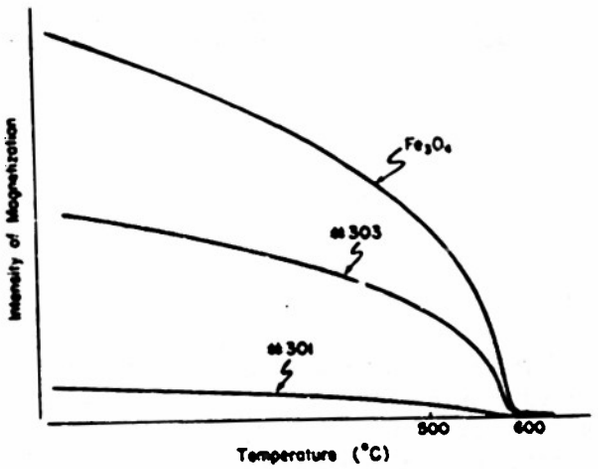

FIG. 4. Thermomagnetic curves for unreduced singly promoted (No. 303, 2.5 mole percent BaO) and doubly promoted (No. 301, 6.02 mole percent Al_2O_3, 0.80 mole percent BaO) catalysts.

Unpromoted

One group of unreduced catalysts studied are identified by the fact that they contain no added promoter. They are distinguishable by the amount of oxidation which occurred during their preparation. As a result, we have a series of iron oxides having various amounts of ferrous and ferric ions. We define γ as the ratio of the number of ferrous to ferric ions. Table II lists the results obtained for the Curie temperatures for a number of these compounds. Data for catalyst No. 973 ($\gamma = 0.50$), is given for comparison. The differences found in the Curie temperatures are not considered to be significant.

Data on the intensity of magnetization, at room temperature, were obtained as a function of the applied field up to about 10,000 oersteds. The measurements were made at the National Bureau of Standards under the direction of Mr. R. L. Sanford. The apparatus used was a high H permeameter.[6] Ti. results are plotted in

TABLE I. Summary of data obtained for singly promoted unreduced catalysts.

Catalyst No.	Composition mole-percent	Curie point (°C)	Intensity of magnetization at room temperature (cgs units)
973[a]	Fe_3O_4	585 (19)[b] ± 1.3	460
210	5.4 Na_2O bal. Fe_3O_4	583 (4) ± 0.75	298
930	2.5 K_2O bal. Fe_3O_4	582 (4) ± 1.0	374
215	0.30 Cs_2O bal. Fe_3O_4	583 (4) ± 0.5	196
303	2.5 BaO bal. Fe_3O_4	583 (4) ± 1.25	246
380	2.4 B_2O_3 bal. Fe_3O_4	582 (4) ± 1.0	264
954	20.4 Al_2O_3 bal. Fe_3O_4	585 (4) ± 1.0	354
956	35.4 Al_2O_3 bal. Fe_3O_4	585 (4) ± 1.5	280
232	15 SiO_2 bal. Fe_3O_4	574 (3) ± 1.25	225

[a] Contains trace of Al_2O_3 that has been neglected.
[b] Numbers within the parenthesis give the number of runs taken. Variations given are the average deviations from the mean without regard to sign.

[6] The apparatus used is described by R. L. Sanford and E. G. Bennett, J. Research Natl. Bur. Standards 26, January 1941.

TABLE II. Summary of data on Curie temperatures.

Catalyst No.	$\gamma = \frac{Fe^{++}}{Fe^{+++}}$	Curie temperature (°C)
909	0.352	585 (3)*±1.0
973	0.500	585 (19)±1.3
918	0.531	582 (3)±0.6
926	0.774	583 (3)±1.6
928	1.276	582 (3)±1.0

* Numbers within brackets are the number of runs taken. Variations given are the average deviations from the mean without regard to sign.

Fig. 5. It is noticed that saturation sets in at about 3000 oersteds. Figure 6 illustrates how the saturation magnetization varies as a function of γ; the maximum occurring at approximately that value of γ corresponding to magnetite.

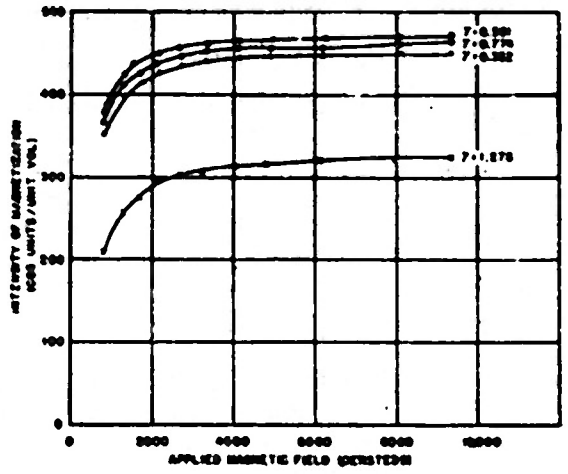

FIG. 5. Relationship between the intensity of magnetization and applied field for various values of $\gamma = Fe^{++}/Fe^{+++}$.

Doubly Promoted

Table III gives the results obtained for the unreduced doubly promoted catalysts, as indicated by the information in the first four and the last columns. These doubly promoted catalysts contained, in all but one case, Al_2O_3 as one component. The second component was one of the single promoters listed in Table I. We find in these data a situation somewhat similar to that found for the singly promoted catalysts: small variations in the Curie point but large variations in the intensity of magnetization. Additions of these various oxides, in every instance, reduced the intensity of magnetization—the Curie point either remained constant or decreased slightly.

In the last column of Table III, we have listed the nature of the slope of the intensity of magnetization vs temperature curves. This terminology refers to the steepness of the slope of the curves in the neighborhood of the Curie point. The curves for the doubly promoted catalysts are classified as having either a steep, flat, or double slope. Figure 7 illustrates examples of a steep and double slope for Nos. 178 and 952 respectively. This distinction has been made because it shows an important characteristic of the material which is not evident when only values for the Curie temperature are given. Two separate phases with different Curie temperatures may show a resultant thermomagnetic curve that has only an approximately flat slope which does not resolve itself into two abrupt reductions in I_s which could be identified as two Curie temperatures.

V. RESULTS ON REDUCED CATALYSTS

Table IV summarizes the data obtained for the reduced catalysts. The Curie temperature obtained for these materials is close to the value for pure iron. Although no calibration measurements were made of the intensity of magnetization of these materials, it was estimated, from the forces developed on the samples studied, that they did not show as great a variability in the intensity of magnetization as found for the unreduced catalysts.

VI. DISCUSSION

The Curie temperature can be expressed[7] approximately in terms of the exchange energy of interaction J

TABLE III. Summary and calculations of data for doubly promoted unreduced catalysts.

Catalyst No.	Composition mole percent	Curie point (°C)	Intensity of magnetization at room temperature (cgs units)			Nature of slope
	Balance Fe_3O_4		Experimental	Calculated	Expt/Calc	
922	2.35 Al_2O_3 0.61 K_2O	583 (4)*±2.5	446	427	1.04	Steep
178	3.80 Al_2O_3 2.27 K_2O	571 (6)±1.7	342	363	0.94	Steep
951	5.07 Al_2O_3 7.98 K_2O	561 582	299	158	1.83	Double slope
952	14.70 Al_2O_3 11.90 K_2O	583±1.5 560	350	0	—	Double slope
383	1.21 B_2O_3 0.48 K_2O	574 (4)±0.5	380	345	1.10	Steep
401	6.35 Al_2O_3 4.25 Na_2O	579 (4)±1.0	185	300	0.62	Flat
234	1.18 Al_2O_3 6.88 SiO_2	576 (3)±0.3	348	347	1.00	Steep
301	6.02 Al_2O_3 0.80 BaO	569 (4)±1.70	31	363	0.08	Flat

* Numbers within the parenthesis give the number of runs taken. Variations given are the average deviations from the mean without regard to sign.

[7] R. M. Bozorth, Bell System Tech. J. 19, 1 (1940).

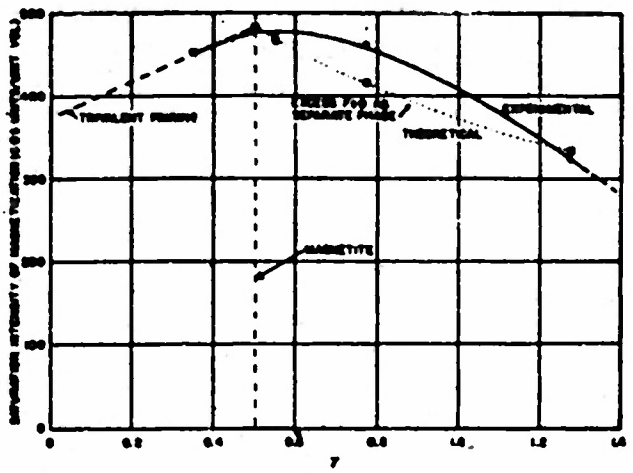

FIG. 6. Variation of saturation magnetization with γ; full curve experimental, broken curve theoretical.

by

$$\theta \sim sJ/k, \qquad (3)$$

where s is the number of nearest magnetic neighbors, and k is the Boltzman constant. It is apparent, therefore, that any loss or gain in the number of nearest neighbors, for a completely homogeneous material,

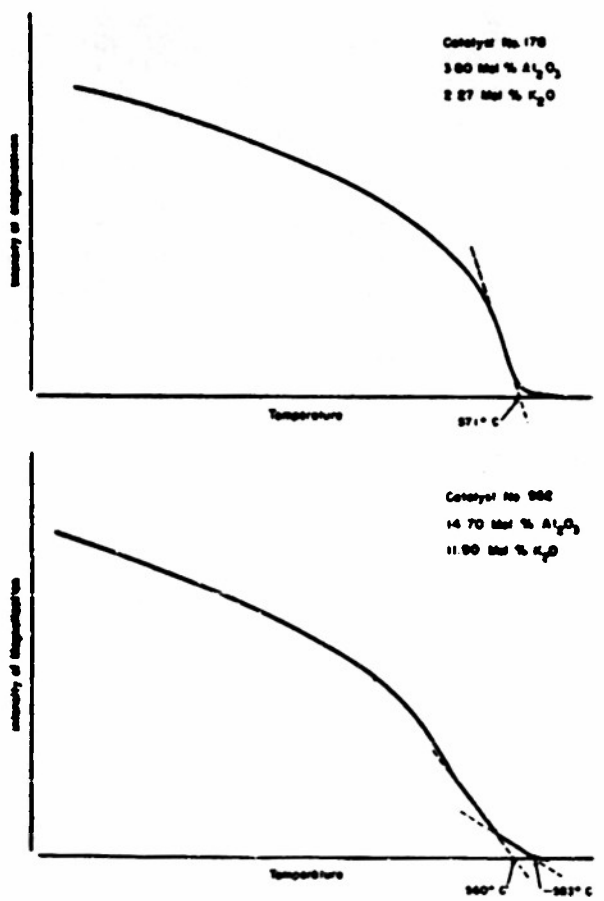

FIG. 7. Thermomagnetic curves of unreduced doubly promoted catalysts illustrating variation of slope with concentration of promoters.

TABLE IV. Summary of data obtained for reduced catalysts.

Catalyst No.	Composition before reduction (mole percent)	Curie point (°C)
973	Fe_3O_4	779 (3)±1.6
954	20.4 Al_2O_3	779 (2)±1.0
930	2.5 K_2O	779 (3)±1.5
178	3.8 Al_2O_3 2.27 K_2O	782 (1)
952	14.70 Al_2O_3 11.90 K_2O	782 (1)
301	6.02 Al_2O_3 0.80 BaO	777 (3)±0.3

should result in a corresponding linear change in the Curie temperature provided that J remained constant.

From Table I we find that, with the exception of the case of catalyst No. 232 containing 15 mole percent of SiO_2, the Curie temperatures of the unreduced catalysts lie within the range 582 to 585°C. The most surprising case of these is No. 954 containing 20.4 mole percent of Al_2O_3. When the amount of Al_2O_3 was increased to 35.4 mole percent, for No. 956, the Curie temperature remained unchanged but the slope of the thermomagnetic curve, as it approached the Curie temperature, showed an indication of a new phase whose Curie point is considerably below that for Fe_3O_4, see Fig. 3.

An intensity of magnetization I (theor) has been calculated on the assumption that the promoters serve only to reduce the intensity of magnetization in proportion to the volume which they occupy. The results of such a calculation are given by Fig. 8. The ratios of the experimental to theoretical values of the intensity of magnetization are plotted with respect to the ionic radii of the metallic ion as given by Goldschmidt. Considering first the case of the addition of Al_2O_3, we have a point indicated by Al^{+++} which was taken from catalyst No. 954 listed in Table I. The intensity of magnetization was found to be nearly proportional to the volume occupied by the Fe_3O_4. Such a situation was not found for the other ions; the greater the ionic radii differ from those for Fe^{++} and Fe^{+++} the greater is the reduction in the intensity of magnetization.

For the doubly promoted unreduced catalysts, we have calculated an intensity of magnetization on the assumption that each of the promoters act independently

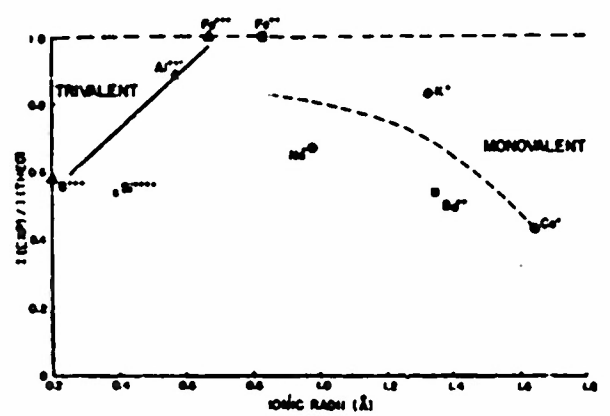

FIG. 8. Correlation of intensity of magnetization with ionic radii for singly promoted catalysts.

in reducing the intensity of magnetization but with the same effectiveness as found when they are used as single promoters. How well such an assumption agrees with the experiment is found in Table III for the values of Expt/Calc listed in the sixth column. We find that this ratio is near unity for catalysts Nos. 922, 178, 383, and 234. For these materials, the slope of the thermomagnetic curve near the Curie point is steep or is a type of curve characteristic of a single magnetic phase. The corresponding Curie points hold near to or slightly less than that for magnetite. When the amounts of Al_2O_3 and K_2O are increased, as for Nos. 951 and 952, the above calculations of the intensity of magnetization are no longer in agreement with the experimental values. The thermomagnetic curves, however, have a double slope, indicating the existence of new phases within these materials. A certain amount of magnetite still persists for Nos. 951 and 952, because the magnetization is not lost until a temperature of 583°C is reached. When K_2O is replaced by Na_2O or BaO, the calculated value of the intensity of magnetization is much greater than the experimental values and the thermomagnetic curve is flat, indicating the existence of at least two magnetic phases.

Catalyst No. 301 was found to have an intensity of magnetization about 8 percent of the calculated value. The presence of BaO in combination with Al_2O_3 has resulted not only in the formation of at least one new phase but also caused a great reduction of the intensity of magnetization at the applied field of about 3000 oersteds.

Wyckoff and Crittenden[1] obtained x-ray diffraction patterns of catalysts Nos. 954 and 955‡ in the unreduced state. For 954 there was an excess of FeO equal to the excess Al_2O_3, while for No. 955 the amount of Al_2O_3 present was sufficient to combine with only one-half of the excess FeO. The x-ray diffraction patterns showed only the magnetite lines for 954, but for 955, lines from FeO were present. The size of the unit cell for 954 was found to be only slightly greater than that for magnetite (918). It was concluded that probably the Al_2O_3 combines with the excess FeO forming ferrous aluminate ($FeO \cdot Al_2O_3$), which goes into solid solution with $FeO \cdot Fe_2O_3$. Failure to find additional lines from $FeO \cdot Al_2O_3$ was explained by the fact that the size of the unit cells of the two materials are nearly equal as estimated from their densities. It was pointed out by Wyckoff and Crittenden, however, that in the case of unreduced magnetite, promoted with silica and zirconia, the promoters are simply finely mixed; and that in the case of the doubly promoted (K_2O, Al_2O_3) unreduced catalysts, potassium aluminate may exist as an "unmixed solid solution." The present thermomagnetic studies of catalyst No. 954 indicate that the promoter, even if it combines to form the aluminate, exists at least partially as a separate phase.

‡ No. 955 was not studied in this investigation.

Michel and Pouillard[6] have made a thermomagnetic and x-ray analysis of Fe_3O_4 with various amounts of Al^{+++} substituted for Fe^{+++}. It was observed that both the Curie temperature and the size of the unit cell decreased linearly, with increasing amounts of Al_2O_3, up to the point where about one ion out of seven of Fe^{+++} was replaced by Al^{+++}. For greater concentrations of Al_2O_3 both the Curie temperature and the size of the unit cell remained constant. The reduction in Curie temperature, proportional to the reduction in number of Fe^{+++} present, is in accordance with Eq. (3). The constancy of both the Curie temperature and the lattice spacing observed by Michel and Pouillard are readily understood as indicating that the additional Al_2O_3 is not held in solid solution but must exist as a separate phase forming an inhomogeneous system.

Since, in the present investigation, the Curie temperature remained constant for the singly promoted unreduced catalysts to within less than one percent of that for Fe_3O_4, with the exception of No. 232, we are led to believe that for the following catalysts not more than about one mole percent of the promoters are in solid solution with Fe_3O_4:

Catalyst No.	Promoter (mole percent)
210	5.4 Na_2O
930	2.5 K_2O
303	2.5 BaO
380	2.4 B_2O_3
954	20.4 Al_2O_3
922	2.35 Al_2O_3 0.61 K_2O

Catalyst No. 232 is partially in solid solution to the extent of about 2 percent leaving approximately 13 percent SiO_2 existing as a separate phase. While No. 956 apparently has a phase in solid solution with Fe_3O_4, judging from the slope of the thermomagnetic curve.

Of the remaining doubly promoted unreduced catalysts there are Nos. 178, 383, and 234 which have similar thermomagnetic characteristics, as discussed previously in reference to Table III. Their Curie temperatures have shifted to values about 2 percent below that for Fe_3O_4 with a steep slope at the Curie temperature. This indicates that for these materials an appreciable amount of the promoters have gone into solid solution with Fe_3O_4 forming a predominant single phase system. Catalysts Nos. 951, 952, 401, and 301, all containing a greater concentration of the promoter than the above group, indicate that at least two phases exist in solid solution.

Reduced Catalysts

For the reduced catalysts it is concluded, for those reported in Table IV, that the promoters exist separately from the magnetic material after it has been reduced to pure iron, in agreement with the x-ray investigations mentioned above.

[6] A. Michel and E. Pouillard, Compt. rend. 227, 194 (1948).

TABLE V. Application of the Néel theory to the binary system $FeO-Fe_2O_3$.

Material	$\frac{Fe^{++}}{Fe^{+++}}$	Interstice: Tetrahedral	Interstice: Octahedral		Net number of unpaired electrons* per unit cell (at saturation and 0°K): Theory	Net number of unpaired electrons* per unit cell (at saturation and 0°K): Experiment
Fe_3O_4	0.50	8 $Fe^{+++}\uparrow$	8 $Fe^{+++}\downarrow$	8 $Fe^{++}\downarrow$	32	32.6
No. 909	0.352	8 $Fe^{+++}\uparrow$	9.30 $Fe^{+++}\downarrow$	6.06 $Fe^{++}\downarrow$	30.7	30.6
$\gamma-Fe_2O_3$	0	8 $Fe^{+++}\uparrow$	13.33 $Fe^{+++}\downarrow$	0	25.7	25.6

* On the basis of five Bohr magnetons for Fe^{+++} and four Bohr magnetons for Fe^{++}.

Binary System $FeO-Fe_2O_3$

The magnetic data given for the unreduced catalysts having variable ratios of ferrous to ferric iron, constitute a basis for studying, in effect, the binary system $FeO-Fe_2O_3$. These data, given in Fig. 6 and Table II, are in essential agreement with similar results obtained by Kopp[9] and Snoek,[10] who found the maximum intensity of magnetization at $\gamma=0.50$ although the maximum was considerably sharper than the one found in the present work. Likewise Snoek[10] found a constant Curie temperature of 585°C for specimens containing between 30 and 65 mole percent Fe_2O_3 which is in excellent agreement with the present data.

These results are of interest in connection with a recent model proposed by Néel[11] to explain the magnetic properties of Fe_3O_4 and $\gamma-Fe_2O_3$. For Fe_3O_4 the 8 tetrahedral holes per unit cell are presumable occupied by Fe^{+++} ions and the 16 octahedral holes are occupied by 8 Fe^{+++} and 8 Fe^{++} ions. Néel has suggested that the trivalent ions in the tetrahedral and octahedral interstices have negative exchange coupling energies, and tend to align anti-parallel, so that at 0°K the saturation magnetization of Fe_3O_4 is entirely due to the divalent ions. Assuming that there is no orbital contribution to the magnetic moment of the Fe^{++} ions, Néel's model predicts a saturation magnetization of 32 Bohr magnetons per unit cell for Fe_3O_4; the experimental value is 32.6.[12]

The crystal structure of $\gamma-Fe_2O_3$ is spinel-like with vacancies occurring in the octahedral holes. Specifically, it is believed that for a cell of 32 oxygen atoms, the 8 tetrahedral holes are filled and that an average of $13\frac{1}{3}$ of the 16 octahedral holes are occupied. All of the Fe ions are trivalent in $\gamma-Fe_2O_3$ and Néel's model of anti-parallel coupling would suggest that the saturation magnetization is due to the unequal numbers of oppositely aligned Fe^{+++} ions. Again assuming the ionic magnetic moment to be due to spin only, one obtains a value of 26.7 Bohr magnetons per cell of 32 oxygen atoms for the saturation magnetization of $\gamma-Fe_2O_3$; the experimental value is 25.6.[12]

The catalyst No. 909 has a composition between Fe_3O_4 and $\gamma-Fe_2O_3$, so that it offers an interesting possibility of checking Néel's suggestion. The saturation magnetization of No. 909 at 0°K was estimated by assuming that its I vs T curve has the same shape as the corresponding curve for magnetite The saturation magnetization, computed in this way, is 30.6 Bohr magnetons per unit cell. Néel's model would predict 30.7. Table V summarizes the above correlation, while the dashed portion of the theoretical curve given in Fig. 6 is shown for comparison with the experimental curve for data reduced to room temperature. For values of γ above 0.5, x-ray diffraction measurements[1] indicate that the excess FeO exists as a separate phase. The x-ray pattern of FeO became progressively stronger as γ increased. To explain the reductions of intensity of magnetization with increasing γ, we simply assume that the excess FeO exists as a separate nonmagnetic phase which gives the dotted curve shown in Fig. 6. The agreement with the experimental results, however, is only fair.

Attempts were made to explain, by the Néel theory, the reduction of the intensity of magnetization of the unreduced catalyst, No. 954. The Al^{+++} was assumed to fit into the lattice without distortions. The agreement was unsatisfactory. If one wishes to accept the idea of pairing of the ferric ions to hold when different types of metallic ions are present, then we would conclude that the failure to find agreement with the experimental result for No. 954 was due to the fact that the Al_2O_3 was not in complete solid solution with Fe_3O_4—a conclusion already arrived at from the value found for its Curie temperature. It is felt that more information is needed as to the crystal structure of the unreduced singly promoted catalyst before applying the Néel concept of spin orientation to this type of material.

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[9] W. Kopp, doctoral thesis (Eidgenössischen Technischen Hochschule, Zurich 1919).
[10] J. L. Snoek, Physica, III, 463 (1935).
[11] L. Néel, Ann. Physik 3, 137 (1948).
[12] P. Weiss and R. Forrer, Ann. Physik 12, 279 (1929).